

DIELECTRIC CONSTANT STUDIES

IV. The Moments of Some Inorganic Compounds

A DISSERTATION

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
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Dielectric Constant Studies. IV. The Moments of Some Inorganic Compounds

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The moments of some inorganic compounds have been determined, some in more than one solvent and the best values are believed to be: for SbCl_3 , 3.12; SbBr_3 , 2.47; SbI_3 , 1.58; AsI_3 , 0.96; AsBr_3 , 1.60; PI_3 , 0.0; AsF_3 , 2.65; and LiClO_4 , 7.84 Debye. The dielectric constant of solid AsF_3 was measured and found to be 5.7. The moments of the molecules measured have been calculated from the

electronegativity of the elements and compared with the measured values. A fair agreement is found with deviations greatest for molecules of highest polarizability and possessing large moments. The electronegativity values were deduced from the measurements of the hydrogen compounds or from their periodic relationship.

THE intimate relationship existing between the properties of a molecule and the electrical symmetry or electric moment has led to the belief that the latter gives considerable information concerning the nature and extent of the forces uniting atoms. Indeed so general has this belief become that the terms polar and nonpolar have often been confused with ionic and covalent. Atomic combinations between like atoms are generally known to be nonpolar and it is also generally accepted that true ionic bonds like those of the alkaline metal halides are strongly polar. A growing tendency may be noted to consider that there is no sharp division between bonds of the ionic and covalent type but, rather, that there is a general transition from one type to the other.

It has been pointed out previously¹ that probably all covalent bonds are nonpolar and that the electric moment may be considered a measure of the deviation of the bonds from the covalent type. The measured values of the moments of simple molecules were so limited that the present study was undertaken in order to extend our knowledge in this direction and thus provide for a more adequate generalization in this field.

* Rewritten from a thesis by Mary G. Malone in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Michigan.

¹ J. G. Malone, *J. Chem. Phys.* **1**, 197 (1933).

PREPARATION OF MATERIALS AND SOLUTIONS

Benzene

The thiophene-free material was stirred with sulphuric acid until it was no longer colored, washed with water and sodium hydroxide solution and stirred with water for some time. The benzene was then dried with calcium chloride and fractionated. The middle portion was fractionally frozen, redistilled from phosphorous pentoxide and dried over sodium.

Carbon disulfide

The c.p. quality was further purified by shaking with mercury until the mercury was no longer tarnished, fractionated, dried by refluxing with phosphorous pentoxide, again fractionated and redistilled just before using. No difference in capacity was noted in the different samples prepared if they were measured just after distilling. After standing for some time, however, a slight change was detected.

Dioxane

Eastman's best quality was further purified by refluxing with sodium, fractionally distilling and standing over sodium. Different samples of dioxane showed different dielectric constants depending upon the length of time it was allowed to stand over freshly cut sodium. Constants for dioxane were redetermined every day it was used.

Carbon tetrachloride

Eastman's best quality was fractionally distilled, dried over calcium chloride and redistilled.

Antimony trichloride

Baker's c.p. grade was purified by fractional distillation under reduced pressure. The distillate was collected in the same vessel in which the solution was prepared so that no moisture was admitted. Benzene solutions so prepared showed no cloudiness.

Antimony tribromide

Coleman and Bell c.p. quality was purified in the same manner as the trichloride. The capacity of the carbon disulfide solutions changed with time, a noticeable change occurring in half an hour. To avoid this the solutions were made at 25° and measurements taken immediately and at short intervals over a period of several minutes. The values obtained in this way did not change during the intervals.

Antimony triiodide

The Eimer and Amend c.p. quality was recrystallized from carbon disulfide. The crystals were light in weight, bright red in color and every face shone with a luster. They did not tarnish when exposed to air for a short time. The carbon disulfide solution of antimony triiodide was clear and yellow in color and did not darken with time. The capacity measurements did not change with time.

Arsenic tribromide

The Eimer and Amend c.p. quality was purified by fractional distillation and collected in the manner described for the antimony chloride. The capacity measurements did not change with time.

Arsenic triiodide

The Coleman and Bell c.p. quality was purified by recrystallization from carbon disulfide. The crystals were red, shiny plates. They were dried from the carbon disulfide by dried carbon dioxide gas and handled in carbon dioxide during use. They were attacked by air, losing their luster. They formed an orange-to-red solution in carbon disulfide in contrast to the

yellow one produced by the antimony compound. The solution turned dark after several days. No change of capacity with time was noted during the time the solution was in the cell.

Phosphorus triiodide

It was prepared by refluxing, for some time, equivalent quantities of phosphorus and iodine dissolved in carbon disulfide. After the reaction was complete the solution was concentrated, cooled, and the red crystals were deposited. They were washed and recrystallized twice. The phosphorus triiodide fumed in the air and had to be handled in a dried carbon dioxide atmosphere. The carbon disulfide solutions were yellow in color and showed no tendency to darken when kept sealed from the air for three weeks. The capacity measurements were constant.

Arsenic trifluoride

It was prepared in a three-compartment dry glass apparatus which was evacuated. Equivalent weights of calcium fluoride and arsenious oxide were placed in the first compartment and a large excess of concentrated sulfuric acid added from a dropping funnel. The arsenic trifluoride formed was distilled into the second compartment, the third compartment being closed from it by a stopcock. The second compartment was closed from the first and the material kept until time for use. At that time a small first portion was distilled into the third compartment. It was removed by a vacuum pump and the middle portion distilled into this compartment for use. Solutions were made by adding the liquid from this compartment directly into the benzene in a dry nitrogen atmosphere. The glass apparatus and cell were only very slightly etched after use and the density bottle to a slightly greater extent. Some AsF_3 was kept in good condition in the glass apparatus for several months.

Lithium perchlorate

A very pure sample was obtained from Professor H. H. Willard. It was dried by fusing.

Iodine monochloride

Eimer and Amend c.p. quality was purified by a fractional recrystallization.

EXPERIMENTAL

A heterodyne apparatus similar to that employed by other workers² in this field was used for the solution measurements. For the solid arsenic trifluoride and iodine monochloride, a resonance apparatus was used, described in a previous paper³ from this laboratory.

Two cells were used for the solution measurements, each consisting of five coaxial gold-plated brass cylinders. The plates of one of the cells were spaced with mica and those of the other with Bakelite. Leads were made to mercury cups. Different capacities could be obtained by using different combinations of the plates. The cells had maximum capacities of about 193 and 183 mmf, respectively. Small cells with platinum plates were used with the resonance apparatus.

The density bottle was similar to that described by Dr. Wooley.⁴ The 33 cc bottle had a 2 cc graduated pipette attached making it possible to take readings at different temperatures with one weighing. An error of 0.03 percent could occur due to the volume reading.

The apparatus was tested by measuring the moment of antimony trichloride in benzene. A value of 3.84 was obtained, which is in good agreement with the values 3.6 by Werner,⁵ 4.11 by Bergman and Engel⁶ and 3.75 to 3.95 by Smith.⁷

In the Tables I to XI inclusive, c_2 represents

TABLE I. Moment of $SbCl_3$ in carbon disulfide at 25°.

$P_{200}' = 205 \quad \mu = 3.12 \pm 0.05$						
c_2	d	ϵ	P_{12}	P_2	P_{E+A}	P_2'
0.000	1.2600	2.634				
0.00243	1.2659	2.692	21.85	238	44	194
0.00451	1.2685	2.731	22.20	217		173
0.00707	1.2718	2.789	22.62	205		161
0.00839	1.2763	2.806	22.77	194		150
0.01281	1.2834	2.913	23.28	181		137
0.01689	1.2930	2.996	24.14	187		143

² Smyth, *Dielectric Constant and Molecular Structure*, p. 54, Chemical Catalogue Company, New York, 1931.

³ J. G. Malone, A. L. Ferguson and L. O. Case, *J. Chem. Phys.* **1**, 836 (1933).

⁴ Wooley, *J. Am. Chem. Soc.* **55**, 3518 (1933).

⁵ Werner, *Zeits. f. Anorg. allgem. Chemie* **181**, 154 (1930).

⁶ Bergman and Engel, *Zeits. f. physik. Chemie* **B13**, 232 (1931).

⁷ Smith, *Proc. Roy. Soc. (London)* **A136**, 256 (1932).

TABLE II. Moment of $SbBr_3$ in benzene at 25°.

$P_{200}' = 225 \quad \mu = 3.28 \pm 0.1$						
c_2	d	ϵ	P_{12}	P_2	P_{E+A}	P_2'
0.000	0.8374	2.276				
0.00404	0.8858	2.351	27.60	273	50	223
0.00512	0.8899	2.369	27.82	267		217
0.00514	0.8900	2.363	27.79	263		213
0.00712	0.8949	2.406	28.40	274		224
0.01270	0.9121	2.495	29.70	269		219

TABLE III. Moment of $SbBr_3$ in carbon disulfide at 25°.

$P_{200}' = 225 \quad \mu = 2.47 \pm 0.1$						
c_2	d	ϵ	P_{12}	P_2	P_{E+A}	P_2'
0.000	1.2600	2.634				
0.002333	1.2691	2.674	21.69	180	50	130
0.003638	1.2745	2.692	21.85	170		120
0.003959	1.2748	2.700	21.92	173		123
0.007421	1.2888	2.757	22.45	172		122
0.013659	1.3120	2.844	23.23	161		111

TABLE IV. Moment of SbI_3 in carbon disulfide.

$P_{200}' = 52.5 \qquad \mu = 1.58 \pm 0.1$							
c_2	T	d	ϵ	P_{12}	P_2	P_{E+A}	P_2'
0.000	25°	1.2600	2.633				
0.001603		1.2706	2.652	21.465	124.8	76.8	48.0
0.001945		1.2731	2.658	21.52	132.9		53.1
0.002140		1.2753	2.660	21.515	124.5		47.7
0.002643	36°	1.2797	2.665	21.56	117.1		40.3
0.000		1.2501	2.610				
0.003944		1.2778	2.662	21.70	129.3		52.5

TABLE V. Moment of $AsBr_3$ in carbon disulfide at 25°.

$P_{200}' = 54.0 \quad \mu = 1.60 \pm 0.05$						
c_2	d	ϵ	P_{12}	P_2	P_{E+A}	P_2'
0.000	1.2600	2.634				
0.002648	1.2685	2.651	21.478	88.0	37.6	51.4
0.005719	1.2793	2.671	21.67	85.7		48.1
0.008448	1.2887	2.689	21.84	85.2		47.6
0.009160	1.2910	2.697	21.91	86.1		48.5
0.010454	1.2960	2.707	21.90	78.4		40.8
0.011953	1.3005	2.713	22.07	85.3		47.7

TABLE VI. Moment of AsI_3 in carbon disulfide at 25°.

$P_{200}' = 19.0 \quad \mu = 0.96 \pm 0.1$						
c_2	d	ϵ	P_{12}	P_2	P_{E+A}	P_2'
0.000	1.2600	2.634				
0.000931	1.2647	2.636	21.329	73.5	59	14.5
0.002160	1.2734	2.648	21.42	78.7		19.7
0.002715	1.2760	2.649	21.46	77.4		18.4
0.004226	1.2831	2.657	21.55	80.5		21.5
0.007914	1.3027	2.679	21.71	74.0		15.0

TABLE VII. Moment of PI_3 in carbon disulfide at 25° .

$$\mu = 0$$

c_2	d	ϵ	P_{12}	P_2	P_{E+A}	P_2'
0.000	1.2600	2.633				
0.001650	1.2682	2.636	21.334	43.83	49.75	0
0.002708	1.2730	2.639	21.380	51.69		
0.004840	1.2832	2.641	21.42	47.52		
0.005079	1.2847	2.644	11.445	51.12		
0.007206	1.2925	2.648	21.51	51.34		

TABLE VIII. Moment of AsF_3 in benzene at 25° .

$$P_{200}' = 145.6 \quad \mu = 2.65 \pm 0.05$$

c_2	d	ϵ	P_{12}	P_2	P_{E+A}	P_2'
0.000	0.8734	2.276				
0.01499	0.8869	2.434	28.71	164.1	26.8	137.3
0.02371	0.8948	2.521	29.78	162.5		135.7
0.02914	0.8997	2.574	30.43	156.5		129.7
0.03535	0.9052	2.641	31.21	155.6		128.8

TABLE IX. Moment of $LiClO_4$ in dioxane at 25° .

$$P_{200}' = 1285 \quad \mu = 7.84 \pm 0.05$$

c_2	d	ϵ	P_{12}	P_2	P_E	P_2'
0.000	1.0310	2.315				
0.002767	1.0345	2.544	28.92	1048	24	1024
0.003970	1.0362	2.620	29.92	990		966
0.004445	1.0370	2.672	30.40	994		970
0.000	1.0310	2.325				
0.0005967	1.0318	2.381	26.88	1258		1234
0.001263	1.0326	2.435	27.60	1172		1148
0.002004	1.0336	2.498	28.37	1133		1109
0.002402	1.0342	2.524	28.68	1106		1082

the mole fraction of the polar substance, ϵ the dielectric constant of the solution, d the density, P_{12} the polarization of the mixture and P_2 the polarization of one solute. P_2 is calculated from the following relationship,

$$P_{12} = [(\epsilon - 1)/(\epsilon + 2)] \cdot (c_1 M_1 + c_2 M_2)/d$$

and

$$P_2 = (P_{12} - P_1 c_1)/c_2$$

where c_1 and c_2 , M_1 and M_2 , and P_1 and P_2 are mole fractions, molecular weights and polarizations of the components.

The P_{E+A} values were obtained from the dielectric constants of the solid polar material obtained in case of $SbCl_3$, $SbBr_3$, $AsBr_3$, AsI_3 and PI_3 from measurements by Schlundt.⁸ The

⁸ Schlundt, J. Phys. Chem. 5, 503 (1901); 8, 122 (1904); 15, 381 (1911).

dielectric constant of solid AsF_3 was measured by the use of the resonance apparatus and found to be 5.7. The P_E value of $LiClO_4$ was obtained from refractive index measurements. An Abbé refractometer was used; therefore this value represents the order of magnitude and not an exact measurement. For use in calculating the P_{E+A} values the density of the solid material was obtained from the literature in all cases except PI_3 and AsF_3 , which had to be measured. The density of PI_3 was found to be 3.89 at 25° and that of AsF_3 , 3.01 at the same temperature as the dielectric constant was measured.

The P_2' value represents $P_2 - P_{E+A}$. The values P_2' were obtained by extrapolating the $P_2' - c_2$ curves to infinite dilution. The moment was obtained from the relation

$$\mu = 0.0127(P_{200}'T)^{\frac{1}{2}} \text{ Debye.}$$

An attempt is made to give an evaluation of the size of the known errors in giving the size of the moment. However, this is only an approximation but given so that other authors may not make use of these values to a greater accuracy than the values justify.

An attempt was made to measure the moment of $HgCl_2$ in benzene. Its insolubility made accurate measurements impossible, but the values indicated a zero moment, although a small moment would not be excluded.

Considerable work was done in an attempt to measure ICl in CCl_4 solution. Just what percent of dissociation one has in such a case is not known. The red solution tarnished the gold plate of the cell during the set of measurements. The solution was kept in an inert atmosphere during use. The temperature and dielectric constant curve of solid ICl was studied by means of the resonance apparatus. A change of dielectric constant with temperature was marked, as is shown in Table X. The reason for such changes is

TABLE X. The change of dielectric constant of solid ICl with temperature.

Temp.	ϵ	Temp.	ϵ	Temp.	ϵ
-48°	7.0	-28°	9.4	-15°	11.3
-40°	7.4	-25°	9.5	-12°	12.9
-37°	8.0	-20°	10.4	-11°	13.7
-34°	8.3	-18°	10.8		

not apparent. Somewhat similar changes in the dielectric constant of the hydrogen halides have been ascribed to the effect of rotational energy.*

TABLE XI. Polarization of ICl in CCl_4 at 25° .

$P_{\infty}' = 60$				
c_2	ϵ	d	P_{12}	P_2
0.000	2.230	1.5837		
0.003423	2.239	1.5863	28.35	58.4
0.005060	2.243	1.5880	28.38	55.9
0.005126	2.244	1.5886	28.39	55.5
0.006238	2.2465	1.5891	28.43	55.1
0.008589	2.251	1.5912	28.47	54.7

Strong electrolytic types of atoms are usually considered to possess high moments. The measurements given here for lithium perchlorate further substantiate this view. It may be that it is even a better case than the silver perchlorate measurement⁹ so often quoted, for Gosh¹⁰ was unable to show complex formation between perchlorates and dioxane.

The theoretical treatment follows that of the work of Malone¹ previously referred to. The electronegativity scale has been extended on the basis of the periodic table, as is recorded in Table XII. The bonds not in parenthesis are

TABLE XII. Electronegativity of non-metallic elements referred to H as zero.

	0.28	0.40
	N 1.04	O 1.32
0.69	P 0.36	F (1.72)
	S 0.63	Cl 1.03
0.26	As 0.10	Br 0.78
	Se (0.37)	I 0.38
0.40	Sb (-0.30)	Te (-0.03)

those taken from the experimental data on the hydrogen compounds. The bonds in parenthesis were obtained by the addition or subtraction of the differences in either the horizontal or vertical columns. For example, the value of F was

* Professor Barker informs us that this is impossible in this case.

⁹ Williams, Phys. Zeits. **29**, 174 (1928).

¹⁰ Gosh, J. Chem. Soc. **107**, 159 (1915).

obtained by adding 0.69, the difference between N and P and between O and S, to the value of Cl to obtain 1.72 for F.

In order to use such a table to calculate moments it must be assumed that electronegativity is an additive property. Also, in the case of several vector moments present in a molecule, the angles present must be known. The reaction of one moment on another is a matter of some importance but its effect is difficult to evaluate. One assumes also that the angles remain constant as long as only two species of atoms are concerned.

It is to be expected in highly polarizable atoms with high moments that considerable discrepancies would be encountered. But it may be assumed that the agreement will be the best in those cases where the conditions most nearly approximate the polarizability conditions prevalent in the hydrides, upon which the table is based. This has proved to be the case and is to be observed, especially in the case of the arsenic fluoride. The agreement of the calculated and the observed value is very good. This value is one of great interest. All modifications of the scale given here indicate that fluorine is an element of greater electronegativity than any other. On this basis, the moment of HF should be greater than the moment of HCl. For the same reason the moment of AsF_3 should be greater than the moment of $AsCl_3$, as was found to be the case. Some recent work by Kirkwood¹¹ has indicated a moment of about 0.8 for HF. Our results require a much higher value. A measurement of the moment of gaseous HF would be very valuable and is contemplated in this laboratory.

Since complexes of benzene and antimony chloride and bromide are formed¹² it is of interest to have values for the moments of these materials in another solvent. Carbon disulfide was selected for the purpose, since there is no evidence available to indicate that complexes are formed with it. The measurements showed only slightly lower moments in each case. These lower values are listed in Table XIII.

The antimony triiodide was measured only in carbon disulfide where its solubility is somewhat

¹¹ Kirkwood, Phys. Zeits. **33**, 259 (1932).

¹² Smith and Davis, J. Am. Chem. Soc. **41**, 411 (1922); Cremer and Duncan, J. Chem. Soc. 2750 (1930).

TABLE XIII. *Calculated and observed moments.*

Mol.	Calc.	Obs.	Refr.	Mol.	Calc.	Obs.
SCl ₂	0.51	0.56	Smith	SbCl ₃	2.23	3.12*
PF ₃	2.01			SbBr ₃	1.81	2.47*
PCl ₃	0.98	0.8	Berg.	SbI ₃	1.14	1.58*
		0.9	Smith			
PBr ₃	0.62	0.61	Berg.	SbH ₃	0.50	
PI ₃	0.0	0.0*		SbF ₃	3.41	
AsCl ₃	1.44	1.97	Berg.	NCl ₃	0.0	
		2.15	Smith			
AsBr ₃	1.05	1.66	Berg.	NBr ₃	0.36	
		1.60*				
AsI ₃	0.43	0.96*		NI ₃	0.92	
AsF ₃	2.53	2.65*		NF ₃	0.97	
IBr	0.40			ICl	0.65	0.9–1.1*

* Work in this laboratory.

Smith, Proc. Roy. Soc. **A138**, 154 (1932); **136**, 256 (1932); Bergman and Engel, Zeits. f. physik. Chemie **B13**, 232 (1931).

greater than in benzene. The value found, 1.58, leads us to believe the value 0.40 ascribed to Williams by Werner¹³ is too low.

The measured moments of the three antimony compounds vary considerably from the calculated ones. It must be borne in mind, however, that these were calculated from the predictions in the periodic table and not on a measured hydride, as was true in the other cases. As was previously mentioned, molecules of high polarizability with high moments should be expected to deviate somewhat from the calculated values and it is borne out in these cases. In predicting a moment for SbF₃ from these data one would place it nearer the calculated value than the other antimony compounds. Its insolubility in nonpolar solvents so far available prohibited a measurement.

Arsenic tribromide was measured in carbon disulfide in order to compare it with the measurements by Bergman and Engel¹⁴ in CCl₄. It is

¹³ Williams and Werner, Zeits. f. anorg. allgem. Chemie **181**, 154 (1930).

¹⁴ Bergman and Engel, Zeits. f. physik. Chemie **B13**, 232 (1931).

assumed that carbon tetrachloride and carbon disulfide are compounds of similar polarity. The agreement is all that could be desired.

In the case of PI₃ one would expect only a very small moment, as the moment of the bond P—I is negligible. This has been found to be the case, the measured moment could not be distinguished from zero.

Any moment calculated from the data given for ICl (if one is justified in making such a calculation) is much higher than the one expected from the bond moments. ICl is another highly polarizable molecule with a reasonably high moment.

CONCLUSION

The evidence presented by the additional measured values of the dipole moments of inorganic compounds indicates the advantages and the limitations of attempting to treat the concept of moments on the basis of electronegativity. It is already indicated that the concepts which this method introduces are not wholly adequate to give quantitatively the moments in some cases. The method on the other hand has the merit of allowing generally recognized but poorly stated concepts to be expressed in terms that are capable of quantitative evaluation. A great mass of dipole moment data has been accumulated, chiefly on complex organic molecules, which if properly interpreted would, no doubt, be of great value. Such interpretations must be based on the fundamental relation of dipole moment to other properties of the molecule and these in the opinion of the authors can only be obtained by adequate study of the simpler cases.

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